1970

Pesticidal Residue Alterations in Potatoes During Processing.

James Michael Solar
Louisiana State University and Agricultural & Mechanical College

Pesticidal Residue Alterations

in Potatoes

During Processing

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Food Science

by
James Michael Solar
B.S., Southeastern Louisiana College, 1965
M.S., Louisiana State University, 1968
May, 1970

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. Joseph A. Liuzzo for the advice and guidance during the course of this investigation. He is grateful to Dr. A. F. Novak, Head of the Department of Food Science, for the opportunity to perform this research in the Department. He wishes to express his appreciation to Miss Frances Bonner of the Harry D. Wilson Feed and Fertilizer Laboratories for technical assistance.

Appreciation is expressed to Humble Oil and Refining Company and especially to Mr. J. Trigg Wood and Mr. Louis L. Hines for allowing the author to earn part of his expenses incurred during his graduate tenure.

Above all, he wishes to acknowledge the constant encouragement offered by his parents that made this study a success.

TABLE OF CONTENTS

		Page
	ACKNOWLEDGMENT	ii
	LIST OF TABLES	iv
	LIST OF FIGURES	v
	ABSTRACT	vi
I.	INTRODUCTION	1
II.	REVIEW OF LITERATURE	3
	A. Detection Methods	3
	B. Pesticidal Residues in Foods	10
III.	MATERIALS AND METHODS	19
	A. Samples	19
	B. Sample Preparation	19
	C. Dosimetry	19
	D. Extraction of Pesticide Residues	23
	E. Florisil Column	25
	F. Gas-liquid Chromatography	27
	G. Thin-layer Chromatography	29
IV.	RESULTS AND DISCUSSION	31
V.	SUMMARY	49
VI.	BIBLIOGRAPHY	51
VII.	APPENDIX	55
VIII.	VITA	75
IX.	APPROVAL SHEET	76

LIST OF TABLES

Tables		Page
1	Average Quantity of Pesticidal Residues in Two Potato Types in Nonprocessed Potatoes	32
2	Average Quantity of Pesticidal Residues in Irradiated and Nonirradiated, Nonprocessed Potatoes . . .	34
3	Average Quantity of Pesticidal Residues Throughout Three Storage Periods	36
4	Average Quantity of Pesticidal Residues in Processed Irish and Sweet Potatoes.	38
5	Average Quantity of Pesticidal Residues from Irradiation of Processed Irish and Sweet Potatoes	41
6	Average Quantity of Pesticidal Residues as a Result of Two Different Processing Applications.	43
7	Average Quantities of Pesticidal Residues in Heat Processed Potatoes, With and Without Water.	45
8	Average Quantity of Pesticidal Residues in Frozen, Blanched and Unblanched Potatoes.	47

LIST OF FIGURES

Figure		Page
1	Experimental Design for Storage and Processing of Potatoes	20
2	Relationship of Absorbance vs. Time for Five Different Positions in the Irradiation Chamber	22
3	Flow Diagram for Extraction and Detection of Pesticide Residues	24
4	Gas Chromatograph Operating Conditions	28

ABSTRACT

Irish and sweet potatoes were spiked with 100 ppm endrin. One-half of the samples were irradiated and all were processed with one of four processing methods (heat processing, with and without water and frozen, blanched and unblanched). Samples were stored 0, 6 and 12 weeks. Analysis detected three pesticidal residues: aldrin, heptachlor epoxide and endrin.

In the control, heptachlor epoxide was significantly greater in Irish potatoes; aldrin was significantly greater in sweet potatoes. There was no difference in the endrin content. There was a significant decrease of aldrin and heptachlor epoxide with irradiation of the control; endrin was not affected.

Aldrin residues were the only ones of the three to be significantly decreased with storage. Irradiation of processed potatoes did not significantly decrease the quantities of any of the pesticidal residues in the samples.

Processing significantly decreased all of the pesticidal residues. Endrin residues were significantly decreased with heat processing. Endrin was also decreased with a combination of blanching and freezing. Aldrin was altered primarily with blanching and freezing and to a lesser extent by heat processing without water. Heptachlor epoxide was equally affected by each of the processing methods.

INTRODUCTION

Man is constantly protecting his food supply against weeds, insects, plant diseases and rodents. Billions of dollars worth of growing crops are lost to these enemies annually. Rodents, insects and molds cause annual losses of 33 million tons of stored grain and rice throughout the world, according to estimates of the United Nations Food and Agriculture Organization. This is a year's supply of food for 150 million people. Losses of stored grain in the United States alone are estimated at 18 million tons.

To be effective as a control agent, a chemical pesticide must first of all be toxic. Only after many years was it recognized that the chemical itself must also be one that could be used without being harmful to man. The first use of toxic chemicals was to kill insects; thus the term "insecticide" has to a greater or lesser degree been applied to all materials used as control agents. The Federal Insecticide Act of 1910 includes both insecticides and fungicides. The Federal Insecticide, Fungicide and Rodenticide Act (1947) uses the term "economic poison" to apply to all three groups, and in addition includes herbicides. The term "pesticide" is now officially used to cover all toxic chemicals, whether used to combat insects, fungi, weeds or rodents and other specified animals.

The trend toward the safer use of insecticides and concern for public health began about 1925. It was started in 1919 by the embargo of a shipment of western pears. Illness had been reported in England as being caused by eating apples from the United States. To meet this

difficulty, the Federal Food and Drug Administration ruled in 1927 that fruit in interstate shipments should not show more than 0.025 grain of arsenic trioxide per pound of fruit (3.57 ppm). The Federal Insecticide, Fungicide and Rodenticide Act of 1947 made state officials and manufacturers aware of the residues and promoted greater care in the handling and use of the dangerous compounds.

In 1954 the Federal Food, Drug and Cosmetic Act was ammended to provide methods for controlling the amount of residues of pesticides on raw agricultural products.

Many common food products contain some pesticidal residues. It was the intent of this study to investigate the effects of various processing methods and gamma irradiation on the quantity of the residual pesticides in sweet and Irish potatoes.

REVIEW OF LITERATURE

Detection Methods

Coffin and McKinley (1963) developed a method for the separation and identification of six common pesticide residues found in some fruit and vegetable crops. The residues were: O-ethyl-O-p-nitrophenyl benzene thiophosphonate (EPN), methyl parathion, parathion, EPN oxon, methyl paraoxon and paraoxon. In their work, these investigators used lettuce, strawberries and apples that had been spiked with the pesticides. They found that the pesticides could be effectively separated and detected by means of two-paper chromatographic systems. Detection was effected with an alkali spray and heat. The investigators were able to detect residues in amounts as low as 1 ug.

Infrared spectroscopy as a rapid nondestructive analytical tool has been found to have a great potential in residue analysis. Susi and Rector (1958) were able to quantitate chlorinated residues with infrared techniques. Blinn and Gunther (1962, 1962a, 1963) published the infrared spectrum from 2 to 25 microns of 67 pesticides.

Using wave-lengths from 2 to 35 microns, Morris and Haenni (1963) were able to characterize 24 common pesticides. They assigned structures to many of the pesticides by using published spectra-structure correlations.

Payne and Cox (1966) believe that infrared spectroscopy is the best method for unequivocal identification of trace quantities of organic compounds. They compared infrared spectroscopy to such methods as nuclear magnetic resonance, mass spectroscopy, gas-liquid chromatography and thin-layer chromatography. The investigators

found that some pesticides often have very similar retention times, which would make resolution and identification with gas-liquid chromatography impossible. By developing a micro-infrared analytical procedure, they were able to detect the presence and identify several pesticide residues. This would have been impossible with any other technique.

Blinn (1963) combined two methods for the isolation and identification of Thimet residues in potatoes. He was able to separate and purify the pesticides with thin-layer chromatography. After the residues had separated on the plates, they were scraped and prepared for micro-analysis with infrared spectrophotometry. His results of detecting extremely small amounts of residues concurred with those of Coffin and McKinley (1963), Payne and Cox (1966) and Morris and Haenni (1963).

Determination of chlorinated pesticide residues by thin-layer chromatography without prior cleanup was developed by Morley and Chiba (1964). It was their aim, with thin-layer chromatography to use it as a cleanup method prior to analysis by gas-liquid chromatography. Secondly, they used it as a rapid screening method for the qualitative and semi-quantitative analysis of pesticide residues. The investigators used the residues of o,p-DDT, p,p'-DDT, and p,p'-DDE. Their conclusions were that the pesticides were clearly separated with no loss observed. The lower limit of detectibility of the DDT isomers was 0.2 ppm; for DDE, 0.1 ppm. When they spiked apples and lettuce with heptachlor, the researchers were able to detect amounts as low as 0.05 ppm with 90% recovery of the pesticide. The authors found

that gas chromatography with an electron capture detector was more sensitive for detection of absolute amounts than thin-layer chromatography. However, in practice a similar order of sensitivity was often achieved, since 1 ml. of extract, equivalent to 0.5 - 5.0 g. of original material, could be spotted. In gas-liquid chromatography some sort of cleanup is generally required to obtain best results, this can be effected with thin-layer chromatography.

Beasley and Ziegler (1970) developed a method for pesticide residue analysis cleanup using silicic acid-glass fiber sheets. They found this method to be more efficient than the florisil column or thin-layer chromatography. Thin-layer plates had too low a capacity, especially when the pesticide concentration was low, or when a large amount of extraneous material was present. The experimental procedure consisted of fortifying 100 g. portions of chopped spinach with 0.1 ppm of (a) aldrin (b) heptachlor epoxide, (c) dieldrin, (d) endrin, (e) lindane, and (f) p,p'-DDT. Comparisons between the florisil column cleanup and silicic acid-glass fiber sheets were made. The sheets were a commercial preparation trademarked ChromAR Sheet (Mallinckrodt). These workers concluded that the ChromAR Sheet method was more effective in pesticide residue analysis cleanup than the florisil column cleanup method. They have requested that the FDA accept this simplified procedure.

The pesticide GC-9160 (1,3,4-metheno-1H-cyclobuta(cd) pentalene-2-levulinic acid, 1, 1a,3,3a,4,5,5,5a,5b,6 decachloro-actahydro-2-hydroxy, ethyl) produced by Allied Chemical was one of the new Kepone derivatives that showed promise in controlling flea beetles, mites,

and bud worms. Westlake et al. (1970) found the pesticide could not be detected by electron capture gas chromatography. They found, however, that it could be converted to Kepone which was easily detectable. As a source of the pesticide the workers used lettuce, cabbage and citrus fruits. Two different gas chromatographic detection systems were used (electron capture and electron conductivity). The results indicated the electron conductivity detector consistently gave slightly higher recoveries. They felt this was due to lack of background interference associated with the electron conductivity detector.

Burke and Holswade (1964) surveyed 87 chlorinated and 26 thio pesticide chemicals. Their field of interest was the improvement of detection of pesticidal residues. Their method of evaluation utilized a microcoulometric detector (MCGC), which is a multiple detection system. They found with the MCGC specificity of the detector for Cl^-, Br^-, and I^- or sulfur was the instruments' greatest virtue. Maximum sensitivity depended on two factors: 1) the smoothness with which the particular MCGC operated, and 2) the extent of sample cleanup. The investigators concluded that levels that could be measured depended on the type of pesticide and food product in question, but that 0.01 ppm is the general level for maximum sensitivity. At extremely lower levels reductions in both quantitative and qualitative accuracy were noted.

Guiffrida and Ives (1964) simultaneously used different detection systems to detect organophosphate pesticide residues in various crops. The effluent from one column was divided evenly between two detectors to obtain dual analysis. A sodium thermionic detector, highly

sensitive to phosphorus compounds, was used to give quantitative recovery data. A flame ionization detector was used to determine the efficiency of the cleanup. The pesticides Diazion, malathion, parathion, Trithon and DDT were used in the investigation. With the sodium thermionic detector they were able to detect residues at levels as low as 0.1 ppm. Paper chromatographic techniques were employed for confirmation of the pesticides tested.

Ives and Guiffrida (1967) continued the work in the development of thermionic detection systems (TD). Samples consisted of triphenyl derivatives of group V (a) elements. Results indicated that thermionic response to group V (a) elements in organic compounds depended on the salt cation used in the TD. The workers concluded that thermionic detection of organonitrogen compounds promises to help fill the need for a sensitive nitrogen detector. They found it especially useful for compounds containing several nitrogen atoms.

Watts and Klein (1962) constructed and modified the electron capture detector described by Lovelock and Lipsky (1960). They found one design that yielded a nearly linear relationship between amount of pesticide injected and the peak area response. The researchers felt the results clearly demonstrated that the use of an electron capture detector cell with conventional gas chromatography permitted the detection of chlorinated pesticides in amounts far below those detectable by colorimetric or paper chromatographic techniques. The electron capture technique was able to measure as little as 0.0001 ug. levels of chlorinated pesticides with accuracy, whereas the other methods required larger amounts. They noted that since so little of

the final sample solution was required for analysis, many duplicate check runs could be conducted on the same sample solution.

Schmit et al. (1963) used tomatoes and tomato products as a source of pesticide residues to develop a rapid method for their determination. They homogenized the tomatoes with hexane, then slurried the extract with silicic acid. The slurry was put into a sintered glass funnel and the pesticidal residues were eluted with hexane. At this point, after concentration, the solution was ready to inject into the gas-liquid chromatograph. The method of Beasley and Ziegler (1970) compared favorably to that of Schmit el al. (1963). Both used silicic acid as the adsorbant, which allowed for elimination of the florisil column cleanup step. The results that each obtained coincided completely. Both groups of authors agreed that cleanups would be more efficient, yeilding greater recoveries, if the FDA would approve this method over the florisil column cleanup method.

Langois et al. (1964) reported that the development of the electron capture detector by Lovelock and Lipsky (1960) gave the chemist a valuable tool for detection of trace amounts of chlorinated insecticide residues. Using the electron capture detector, Langois et al. (1964) developed a rapid cleanup of dairy products for analysis of chlorinated insecticide residues. Butter, cheese, dried milk, cream, evaporated milk and whole milk were used in the experimentation. Each of these dairy products were spiked with DDT, lindane, heptachlor, dieldrin and endrin. The rapid cleanup method consisted of grinding the dairy product with the pesticides in florisil. The florisil was placed into a column and was eluted with 20% methylene chloride in

petroleum ether. The eluants obtained were pure enough to be injected into the gas-liquid chromatograph. This method was a major breakthrough in pesticide residue cleanup of dairy products. Previous to this time all of the fats had to be saponified, which limited the quantity of samples that could be analyzed per day and the amount of residues that could be recovered.

Using a gas-liquid chromatograph with an electron capture detector, Glotfelty and Caro (1970) were able to detect artifacts of the insecticide dieldrin. They found two artifacts in the green leaves of alfalfa, wheat, corn, kale, clover, but not in soil, water or nongreen plant parts. They found that the substances were extracted along with dieldrin in the usual cleanup procedure. When the extract was injected into a gas-liquid chromatograph a completely symmetrical "dieldrin" peak with no base-line broadening was produced. The artifacts were completely disguised. With the artifacts appearing in the dieldrin peak, quantitation was impossible. They developed two methods to remove the artifacts from the dieldrin extract. Thin-layer chromatography with unactivated silica gel was found to be effective in removing the artifacts. Saponification with KOH as a part of the cleanup procedure completely destroyed the artifacts. This procedure was the only completely satisfactory cleanup procedure for dieldrin. This method gave excellent cleanup and permitted correct identification and quantitation of dieldrin residues at levels of 0.01 ppm or above. The researchers also were able to tentatively identify the artifacts as nonhalogenated, pigment related natural products found only in photosynthetic tissue. Positive identification was not made, because the compounds were not stable when isolated.

Pesticidal Residues in Foods

Gannon et al. (1959) studied the storage of dieldrin in tissues of cattle and its excretion in milk. They stated that the chlorinated hydrocarbon insecticides have long been known to be stored in animal fat to varying degrees. The extent of the usage of these insecticides on forage crops depends greatly on their propensity for storage in fat and/or their excretion in milk. A few insecticides have been assigned tolerances in the fat of certain animals, but to date (1959) regulatory agencies have tended to maintain that milk is not to be contaminated by pesticides or other substances.

Some research has been done by Claborn and Wells (1952), Ely et al. (1954) and Harris et al. (1956) which indicated that dieldrin was excreted in milk at fairly high levels when cows were sprayed or fed at fairly high dosage rates.

The study of Gannon et al. (1959) was initiated to determine whether or not there was a level of feeding below which contamination of fat, and especially milk of dairy cows would not occur. The cows in the study were first on a control diet that contained no pesticides. Before the cows were put on a dieldrin diet, both the rations and the milk samples were analyzed to insure they contained no dieldrin residues. Once this was assured the cows were fed dieldrin at levels of 0.1, 0.25, 0.75, and 2.25 ppm for 12 weeks. Measurements of dieldrin levels were performed for 18 weeks after the feeding study had begun. At the end of the 12 week period, dieldrin was present in the milk in measurable quantities at all levels of feeding. The workers found a direct relationship between the fatness of the animal and the amount

of dieldrin appearing in the milk. The same was found for the amounts of dieldrin stored in the fat.

Steaks and roasts from cows which had been fed high dosages of dielrin were cooked and compared for dieldrin content with similar raw cuts. No significant losses of dieldrin due to cooking were evident.

Henderson and Crosby (1968) investigated methods of photodecomposition of dieldrin residues in water. They fortified water samples with dieldrin and stored the sample in sunlight for three months. Other samples were stored in the dark to serve as controls. The investigators found that 1/3 of the dieldrin had been decomposed in the samples stored in sunlight. Further investigation, however, revealed that a photoisomer had been produced in its place and was detectable with gas-liquid chromatography. In the control samples no isomers were produced.

Changes in pesticides in canned spinach were studied by Farrow et al. (1966). Using chromatographic procedures for the analysis of pesticide residues in various canned foods, the authors occasionally observed traces of TDE. The investigators suspected that this compound resulted from DDT breakdown during processing or storage of canned products, since DDT could be present as a legal residue.

Canned spinach from a local market was used in the experimentation. Initial analysis indicated the presence of p,p'-TDE. DDT was added to the spinach and then it was recanned, simulating commercial processing conditions. Qualitative and quantitative determinations were performed to confirm the validity of the conversion of p,p'-DDT to p,p'TDE. Results showed that both p,p'-DDT and p,p'-TDE were present

in all samples. The DDT losses ranged from 10 to 20% and TDE increased in proportional amounts.

Saha et al. (1970) spiked rapeseed flakes with lindane- and DDT- ^{14}C. The rapeseed was processed in the laboratory simulating actual commercial conditions. Six stages (cooking and oil extraction, desolventization, refining, bleaching and deodorization) of processing were performed on the product. After each stage, sample aliquots were taken and analyzed with a scintillation detector.

Labeled compounds were used for two reasons. First, errors involved in the determination of low levels of residues in oil by electron capture gas chromatography were expected to be higher than those in the determination of radioactivity in the oil. Second, it was not known whether any of the processing techniques would convert lindane or DDT into any other fat soluble product(s) which might escape detection by gas chromatographic procedure. Determination of radioactivity in the processed oil included lindane- or DDT- ^{14}C and any possible degradation product(s). Also, 100% recoveries were obtained with this method.

Cooking of rapeseed flakes removed 96.4% of the lindane and 95.5% of the DDT. The residues were transmitted to the oil fraction. None of the other processing procedures removed a significant amount of the pesticides from the oil, except for the deodorization step. This phase of processing had a highly significant effect on the pesticidal residues. Lindane- ^{14}C had a 95.3% loss and DDT- ^{14}C incurred a 98.3% loss.

Studies concentrated on the removal of DDT, parathion, and carbaryl from spinach by commercial and home preparative methods were

performed by Lamb et al. (1968). The workers obtained treated samples and processed part of them under commercial conditions and the remainder under home preparative procedures. Home preparation consisted of home cooking, freezing and canning. Sample analysis was performed during each phase of both preparative procedures.

Results of the experimentation showed no significant differences in residue levels of DDT and parathion after 15 and 13 days storage, respectively. Minimum and maximum commercial washing removed 17 and 48% of the DDT, 0 and 9% of the parathion, and 66 and 87% of the carbaryl. Use of a detergent in the wash water increased the percent removal. After commercial water blanching, 38 to 60% of the DDT was removed, 49 to 71% of the parathion, and 96 to 97% of the carbaryl. Steam blanching removed little or no residue. After commercial canning and storage for 5 months, no DDT remained, but small amounts of TDE and DDE were found; parathion and carbaryl did not change. These findings concurred with those of Farrow et al. (1966). The p,p'- isomer of DDT decreased more than the o,p'- isomer during washing and blanching. Home and commercial washing removed comparable amounts of DDT and carbaryl. Little or no change in residue occurred after cooking washed spinach without the addition of water.

Hemphill et al. (1967) studied the effects of home preparation techniques on pesticide residues in green beans. The samples were thoroughly washed and trimmed. Three different cooking techniques were used in the experimental design. The beans were either boiled, cooked in a pressure cooker, or cooked in a microwave oven. The green beans and cooking water were analyzed separately. The researchers were able

to detect p,p'-DDT, o,p-DDT, p,p'-DDD, p,p-DDE, o,p-DDD and trace amounts of heptachlor epoxide, dieldrin and endrin. All levels of pesticides were within the tolerances set by the Food and Drug Administration.

Washing reduced the total pesticide residues in green beans by an average of 5.3%. Trimming had very little effect on the pesticide level. The two procedures (washing and trimming), however, caused a mean reduction in the total amount of pesticide by 9.2%. Washing, trimming, and cooking green beans reduced the mean total pesticide residues by 47.1% to 62.9%. The greatest effect (62.9%) was observed in the pressure cooked samples.

Another group of researchers (Carlin et al., 1966) studied the pesticidal residues in green beans. Reports of pronounced "musty" or "earthy" flavors in different crops grown and processed under widely varying conditions, dramatized the necessity for study of each pesticide on various crops and under many conditions of application. Investigations were made using DDT and Guthion to determine: 1) the influence of simulated commercially acceptable processes for canning or freezing upon the magnitude of insecticides remaining after storage for 11 months; and 2) the effect of the insecticide residues on the flavor and quality of the processed beans.

Harvested, treated beans were initially washed, cut and blanched. The samples to be frozen were immediately frozen; the canned samples were placed into cans and heat processed.

After processing and 4 months storage at 0°F., the results showed a lower level of Guthion as compared with the control. Unwashed beans

stored for 11 months at 0° F. showed decreased amounts of DDT. The residues of DDT found on the unwashed beans were considerably less than the FDA tolerance level. The samples that had been canned and heat processed showed a 20 to 27% reduction in DDT level. Fleck and Haller (1946) reported that small amounts of iron would catalytically decompose DDT. Carlin et al. (1966) felt that much of the DDT reduction in the canned samples was attributable to this fact. They felt the presence of iron had more effect on the DDT content reduction, than the heat involved in processing. They also proposed that the heat may have supplied the necessary energy to catalyze the reaction of DDT with iron.

Sensory evaluation of the green beans indicated that the flavor was not affected by the small residues of DDT and Guthion found on the frozen beans, since the judges were not able to distinguish between the flavor of untreated and treated beans. Also, no off-flavors were reported.

Killgore and Windham (1970) reported the disappearance of malathion residue in broccoli during cooking and freezing. The purpose of the experiment was to determine the residue levels resulting from sprays applied at different intervals before harvest and to determine to what extent the residues were removed by cooking or by storing at -9° C. for six months. Broccoli plants were harvested at intervals of 1, 2, 3, and 4 days following malathion application. The broccoli was cooked in boiling salted water. Samples to be frozen were blanched in steam for 5 minutes, sealed in plastic bags with little air space, frozen and stored at -9° C. for 6 months. Broccoli harvested 1 through 4 days

following application contained malathion residues of 10.3, 8.2, 5.4, and 4.5 ppm, respectively. The samples after cooking showed losses of 9, 34, 8.1, and 7.2% malathion from the 1 through 4 day harvest period, respectively. Disappearance of the residue varied from 36 to 90% in samples stored at -9° C. for 6 months.

Endrin persistence on cabbage was studied and reported by Mattick et al. (1963). The cabbage used in the analysis was obtained from different field plots sprayed at rates of 0.8, 0.5, and 0.25 pounds endrin per acre. Samples from each plot were harvested at intervals of 0, 1, 3, 5, 7, 10, 14, and 21 days after application. The amount of endrin in both 0.8 and 0.5 pound per acre samples showed a definite rise between 0 and 1 day after spraying. The 0.25 pound per acre, 0 day sample was lost during laboratory preparation of the samples. Following the initial rise at 1 day, endrin disappeared progressively until 21 days after spraying when the level of endrin was 0.13 ppm or less in all analyses attempted.

Farrow et al. (1968) compared the effects of commercial and home preparative methods on the removal of DDT, malathion, and carbaryl from tomatoes. A field of growing tomatoes was divided into 3 plots. Each plot was sprayed with either DDT, malathion, or carbaryl. Samples were divided into two groups and were prepared by either simulating commercial or home preparative procedures. Residue determinations were made at appropriate points throughout the processing. DDT residues on unwashed tomatoes showed no significant differences with 7 days storage. There was no significant difference with storage of unwashed tomatoes containing malathion, even though there was an

apparent decrease of 30%. Carbaryl also did not show a significant change after 7 days storage.

Commercial preparative methods showed that the wash water removed 85 to 92% of the DDT. Peeling removed 99%$^{+}$ of the DDT and 80 to 94% of the malathion. Carbaryl followed the trend of the other two pesticides with as much as 92% removed by peeling. The investigators could not find any significant differences between the commercial procedure and the home preparative methods.

Elkins et al. (1968) performed the same study as Farrow et al. (1968) with the exception of using green beans instead of tomatoes. Commercial water blanching removed more than 50% of the DDT residue. Additional commercial processing removed approximately 33% of the DDT residue. During home preparative methods, cold water washing and home canning removed a total of 80% of the original DDT residue. During commercial heat processing and home canning methods p,p'-DDT was converted to p,p'-TDE. Commercial processing methods removed more than 94% of the original malathion residue. During home preparative procedures cold water washing removed 96% of the malathion. Only trace amounts remained in home cooked green beans. Commercial water blanching removed 68 to 73% of the carbaryl residue from the beans. Further processing removed no additional carbaryl. Home preparative procedures reduced carbaryl residues to trace amounts.

Lamb et al. (1968) reported on the behavior of DDT in potatoes during commercial and home preparation. The experimental design was the same as reported by Elkins et al. (1968) and Farrow et al. (1968). Low concentrations of o,p'-DDT, p,p'-DDT, and p,p'-DDE were present

at harvest. Commercial washing operations removed about 20% of the total DDT residue from potatoes and lye peeling plus washing removed about 94%. Commercial processing further reduced the residue to insignificant levels. During home preparative procedures, peeling removed more than 91% of the residue.

There was no significant decrease from the original residue when potatoes with skins were boiled or pressure cooked. Potatoes stored at 45° F. for a period of 6 weeks showed no significant loss of residue.

Pentachloronitrobenzene (PCNB) residues in potatoes were studied by Gorbach and Wagner (1967). The potatoes had been grown in PCNB treated soil. The majority of the residue was found in the peel and in the 1 to 2 mm. thick cellular tissue underneath the peel. Under sterile conditions only PCNB was found; however, in potato homogenates that had been allowed to ferment, two metabolites in addition to PCNB were present. The researchers were able to isolate and identify one of the metabolites. The experimental evidence indicated the compound to be pentachloroaniline.

MATERIALS AND METHODS

Samples

Samples of Irish potatoes and sweet potatoes were used in the investigation. Both types were commercial grade obtained from a local supermarket. The Irish potatoes were grown in Idaho and the sweet potatoes in Louisiana.

Sample Preparation

The potatoes were soaked in tap water to remove the excess dirt on the surfaces. They were then peeled and allowed to soak in fresh water. The soaking kept browning from taking place before the potatoes could be placed into containers. Before canning, the samples were coarsely ground in a food chopper. The ground potatoes were thoroughly mixed in order to obtain homogeneous samples. Two hundred grams of ground potatoes were placed into No. 1 metal cans. One milliliter of endrin (100 ppm) dissolved in petroleum ether was introduced into the center of the potatoes in each can. Figure 1 illustrates the design of the experiment.

The samples that were processed with water had 25 ml. of tap water introduced into each can. The blanched samples were placed into a covered container of boiling water and blanched for 15 minutes. All cans were then hermetically sealed. The heat processed group was placed into a retort and heated at 235° F. under 10 psig for 30 minutes.

Dosimetry

Samples that were to be irradiated were separated and irradiated at the Nuclear Science Center at Louisiana State University. The

Figure 1

Experimental Design for Storage and Processing of Potatoes

Storage: 0, 6 and 12 weeks

Potatoes: Irish or Sweet

Irradiated		Nonirradiated	
Heat Processed	Frozen	Heat Processed	Frozen
1. 25 ml. water	1. Blanched	1. 25 ml. water	1. Blanched
2. No water	2. Unblanched	2. No water	2. Unblanched

Gamma radiation source used was a 19,850 curie Cobalt-60 irradiator.

The Fricke Dosimetry Method was used for determining the amount of radiation which would be absorbed from the Cobalt-60 source (Weiss, 1952). The dose rate was measured on the basis of a ferrous ammonium sulfate solution and spectro-photometric determination of the ferric ion produced. Samples of dosimetry solutions were placed in the radiation field for precisely measured lengths of time. After removal of the specimens from the radiation field, their optical densities were determined immediately in a Beckman Type DB Spectrophotometer at wave length 305 millimicrons. A portion of the unirradiated ferrous solution was used as a blank in the spectrophotometer. From the optical density of the irradiated solutions, the radiation dosage was determined from a calibration curve and the following empirical formula:

$$D = 2.94 \times 10^4 \ (1 - 0.007) \ (t - 20)(A/T)$$

where

D: Dose rate

t: Ambient room temperature

A: Absorbancy

T: Time of radiation, minutes

Figure 2 shows absorbancy vs. time curves for the irradiation of the Fricke dosimetry solutions for three time periods: 5 minutes, 10 minutes and 15 minutes of irradiation. The five different curves in Figure 2 represent five different positions in which the dosimetry solutions were placed in the diving bell used to house the food which was irradiated. It is seen in the figure that the absorbancy is linearly proportional to the time of irradiation of the solution.

The temperature of irradiation, t, the absorbancy, A, and time of irradiation, T, necessary to give an absorbancy of 1.0 were the

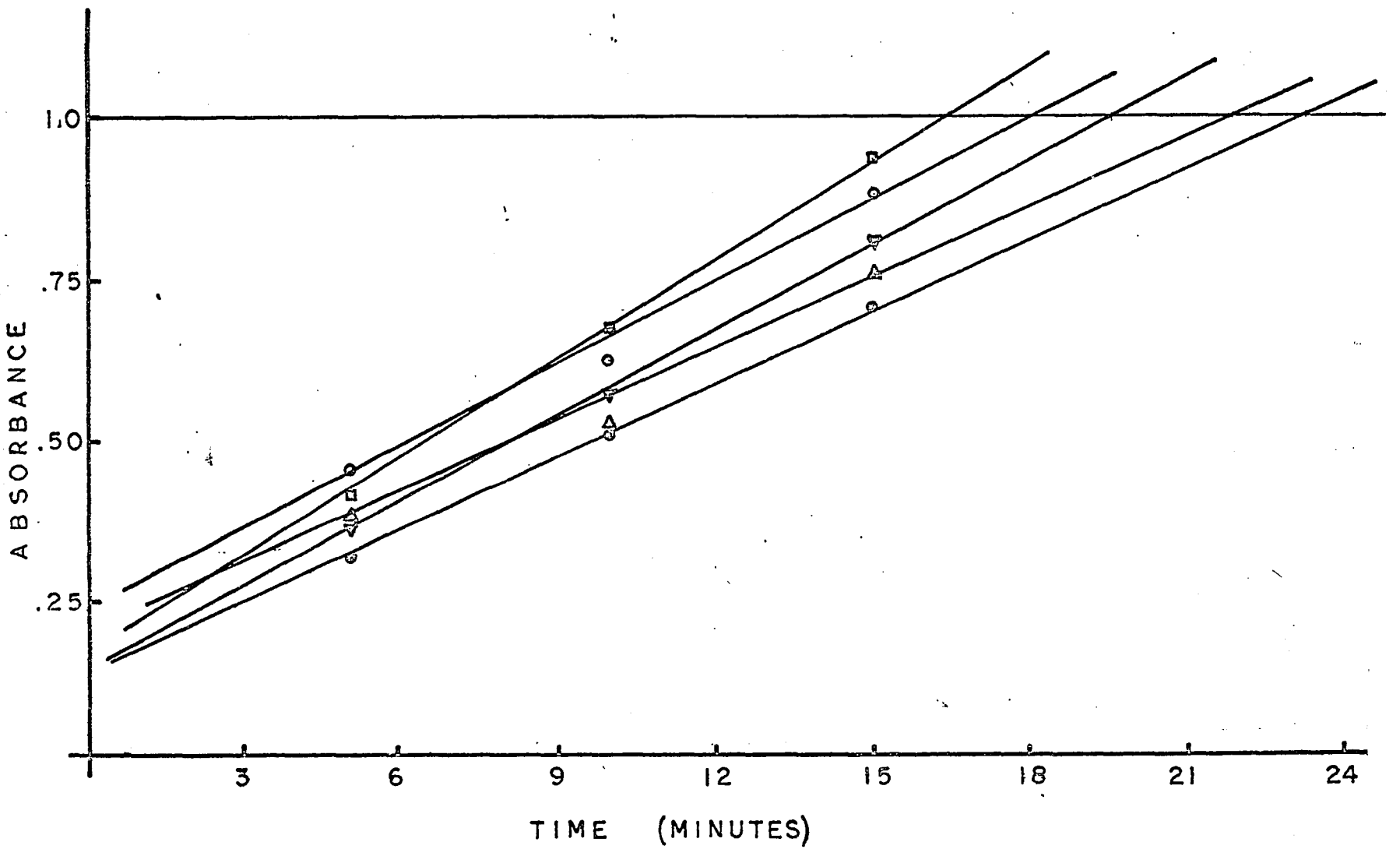


Figure 2. Relationship of Absorbance vs. Time for Five Different Positions in the Irradiation Chamber.

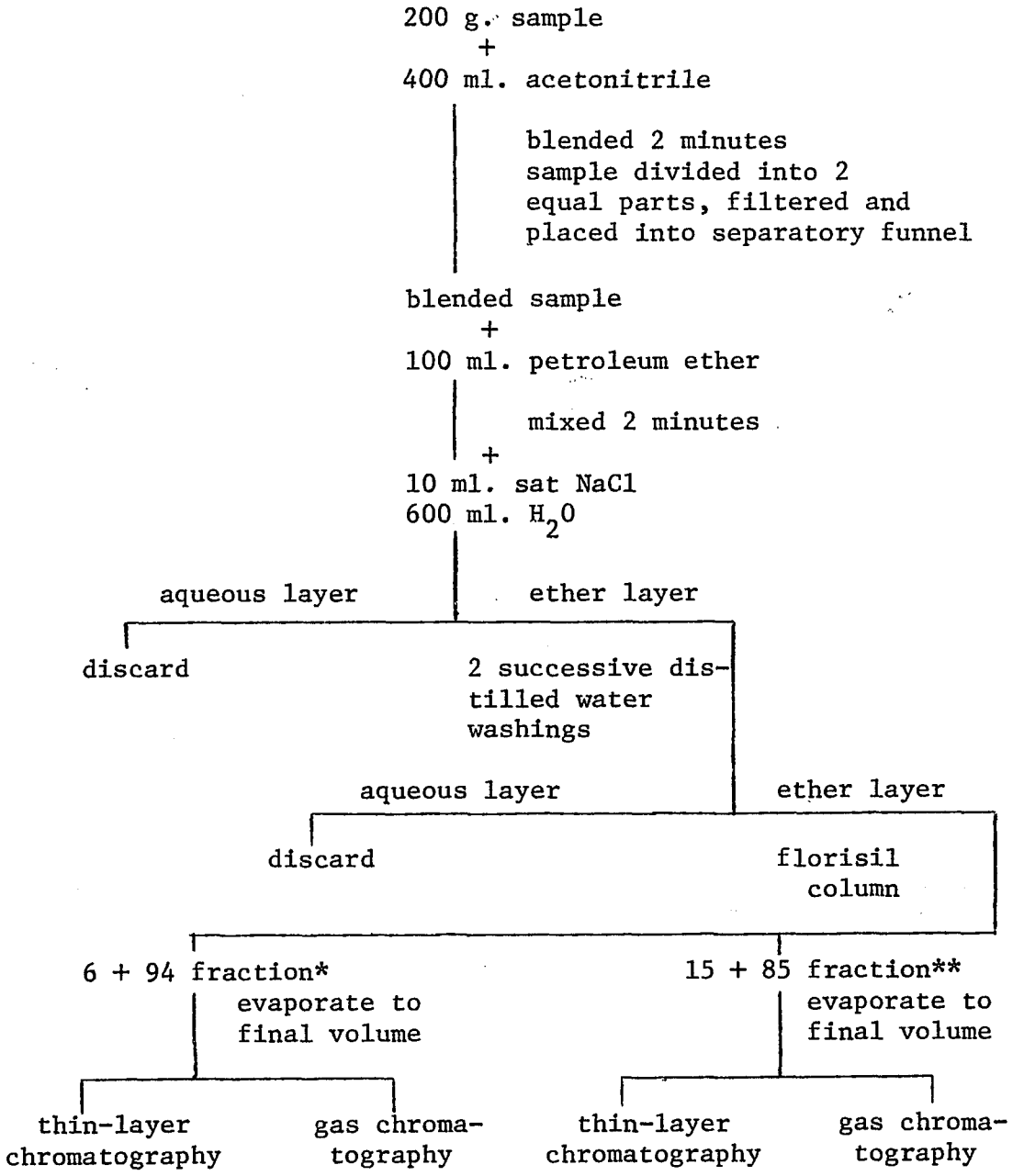
necessary factors inserted into the emperical formula of the Fricke dosimetry method. The length of time required to give an absorbancy of 1.0 was obtained by extrapolation of the absorbancy vs. time to the 1.0 absorbancy line (Figure 2). By inserting the extrapolated values for the time and using the absorbancy of 1.0 and an ambient temperature of 25° C. in the formula, five different dose rates for the five different positions of the Fricke dosimetry solutions were obtained. The mean value of the five determinations was calculated to be 87,258 rads/hour. The potatoes were irradiated for a total of 1 hour and received a dose of 0.087 million rads (Mrad).

Extraction of Pesticide Residues

Extraction of the pesticidal residues was performed as shown in Figure 3. Each can was opened and the contents emptied into a 1000 ml. blendor jar. Four hundred milliliters of nanograde acetonitrile was placed in the jar along with the potatoes and the contents were blended for two minutes. The jars were emptied into a large funnel containing a loose plug of glass wool. The filtrate dripped into a 250 ml. graduated cylinder. The volume of liquid obtained was divided into two parts so that each part represented 100 g. of sample. Each volume was recorded (F). The filtrate was transferred to a 1000 ml. separatory funnel. One hundred milliliters of nanograde petroleum ether (R) were added to the separatory funnel. The petroleum ether was measured in the same graduated cylinder used to collect the filtrate. The contents were vigorously shaken for two minutes to insure transfer of the pesticide residues from the acetonitrile-water layer to the petroleum ether layer. Ten milliliters of saturated sodium chloride

Figure 3

Flow Diagram for Extraction and Detection of Pesticide Residues



*6% ethyl ether in petroleum ether

**15% ethyl ether in petroleum ether

and 600 ml. of distilled water were added to the separatory funnel. The contents were mixed gently, but thoroughly. Ample time was given for the layers to separate, then the aqueous layer was discarded. The solvent layer was washed with two successive 100 ml. portions of distilled water. The washings were discarded and the solvent layer transferred to a 100 ml. graduated cylinder. The volume was recorded (P). Just prior to the florisil column cleanup, 15 g. of anhydrous granular sodium sulfate was added to the petroleum ether extract to absorb the water.

Volumes (F, R, and P) were recorded in order to determine the amount of sample represented by the eluants. This formula was used for the calculation:

Sample represented by eluants = S x (F/T) x (P/R); (1)

where S = g. sample taken; F = volume of filtrate; T = total volume (ml. water contained in sample + ml. acetonitrile added - correction in ml. for volume contraction); P = ml. petroleum ether extract; and R = ml. petroleum ether used to dissolve residue.

Florisil Column

A glass column 60 cm. long, with an inside diameter of 2.5 cm. and a teflon stopcock was used for the column chromatography. Florisil (60 - 100 mesh) was used as the adsorbant. The florisil was activated by placing the adsorbant in a porcelain casserole and heating at 650° C. for 2 hours in a muffle furnace.

The bottom of the column was filled with glass wool to keep the adsorbant in the column. Four inches of florisil was placed in the column and topped with 1/2 inch anhydrous granular sodium sulfate. The column was prewet with 30 ml. nanograde petroleum ether. The

petroleum ether extract from the 100 ml. graduated cylinder was transferred to the column and allowed to flow through at a rate of about 5 ml. per minute. The graduated cylinder was washed with 2 successive 5 ml. portions of petroleum ether. The walls of the chromatographic tube were washed with a small portion of petroleum ether.

The column was eluted with 200 ml. of eluting mixture (6 + 94). This mixture was prepared by diluting 60 ml. of anhydrous purified ethyl ether to 1000 ml. with nanograde petroleum ether. Twenty-five grams of anhydrous granular sodium sulfate were added to remove any water in the mixture. This fraction was collected in a separate collection vessel and labeled "6 + 94" fraction.

The second fraction collected was labeled "15 + 85" fraction. This eluting mixture was prepared by diluting 150 ml. of purified anhydrous ethyl ether to 1000 ml. with nanograde petroleum ether. Twenty-five grams of anhydrous granular sodium sulfate were added to remove any water. Two hundred milliliters of this mixture were used as the second elution solvent. This fraction was collected in a separate container.

Both fractions collected from the column were placed into a warm water bath (45° C.) and evaporated to about 10 ml. During the drying process the walls of the containers were periodically washed with petroleum ether in order to keep the residues from adhering to the walls and in solution. The solutions were transferred to 25 ml. volumetric flasks that had been pre-rinsed with petroleum ether. The volumetric flasks were brought up to final volume. These solutions served for injection into the gas-liquid chromatograph. They were also utilized in the thin-layer confirmative studies.

Gas-liquid Chromatography

Pesticide residue analysis was performed by means of a Varian Aerograph Series 1200 Gas-liquid Chromatograph, equipped with an electron capture detector. The operational conditions employed for the analysis are shown in Figure 4.

The column was pre-conditioned at 250° C. and nitrogen gas with a flow rate of 100 ml. per minute passed through the column. During this time the column was disconnected from the detection port. The detection port was capped to keep any contaminants from entering. After 24 hr. the instrument was ready to perform the analysis.

The samples were injected into the gas chromatograph in amounts varying from 1 ul. to 8 ul. Four replications of each sample were performed. The pesticidal residues were identified by means of standards that were injected into the instrument after the unknown samples were detected.

The standards were prepared by weighing 50 mg. of the material and diluting to 100 ml. with petroleum ether. This was kept as the stock solution. Working standards were prepared from the stock solution giving the following final concentrations:

Heptachlor epoxide	1 nanogram/microliter
Aldrin	1 nanogram/microliter
Endrin	2 nanograms/microliter

Qualitation was performed by means of comparing retention times of the standard to the unknown. Retention time was considered as the time elapsed between the injection and the zenith of the peak.

Quantitation of the pesticidal residues was achieved by determining the areas of the peaks as compared with that of the known

Figure 4

Gas Chromatograph Operating Conditions

Column substrate	Anakrom ABS 90-100 mesh
Column support	10% Dow Corning silicone Fluid DC 200
Column length, shape	6 feet, coiled helix
Column diameter, ID	4 mm., glass
Carrier gas	Pre-purified dry nitrogen
Carrier gas pressure	50 psig
Carrier gas flow rate	120 ml./min.
Operating temperature	
inlet	210° C.
column	200° C.
detector	210° C.
Attenuation	1 - 16
Range	1
Detector	Electron capture
Recorder	Leeds and Northrup, Speedomax H
Chart Speed	1 inch per min.

standard. Actual measurement of the areas was accomplished with the use of a planimeter (Model 39231, Compensating Polar Planimeter, Gelman Instrument Co., Ann Arbor, Michigan).

After the peak areas were determined, they were converted to standard areas. The amount of sample represented by the eluants as calculated by formula (1) was adjusted to 100 g. of sample; the area was likewise adjusted proportionately. For example, if it was determined that a peak area of 100 was represented by 80 g. of sample, the peak area was adjusted to 125, thus representing 100 g. of sample (the standard amount).

Thin-layer Chromatography

Glass plates (20 $cm.^2$) used in thin-layer chromatographic procedures were thoroughly cleansed with detergent and rinsed first with tap water then with distilled water. Immediately before applying the stationary phase, the plates were scrubbed with acetone.

Forty grams of aluminum oxide-G was weighed into a 250 ml. centrifuge bottle. To this, 80 ml. of 0.2% HNO_3 (prepared with double-distilled water) was added to the powder and shaken until the mixture thickened. The slurry was centrifuged at 1500 rpm for 3 min. and the supernatant decanted. The Al_2O_3 was then washed three successive times with 80 ml. double-distilled water. Each time, the slurry was centrifuged and the liquid decanted. Ten milliliters of 1% silver nitrate and enough ethanol were added to make the weight about 110 g. over the weight of the centrifuge bottle. The mixture was then shaken gently to produce a smooth, uniform slurry. The slurry was poured into a spreader previously set at 0.25 mm. thickness and spread evenly over

the surfaces of 5 plates. The plates were air dried for 15 min. and then they were placed in an oven at 100° C. for 15 min. They were immediately stored in a dessicator until needed.

As the plates were used, they were first activated for 15 min. in a 100° C. oven. After cooling to ambient temperature in a dessicator, the extracted pesticidal residues and the standards were spotted separately on the plates. Amounts spotted varied from 0.01 ul. to 0.15 ul. Nine to 12 spots were spotted across the thin-layer plates.

A developing tank was prepared by lining the sides with filter paper and adding N-heptane to the bottom. Ample time was allowed for the solvent to saturate the atmosphere (30 min.). The spotted plates were placed in the tank and resolved until the solvent front reached 1 cm. from the top. The plates were then air dried.

For detection the plates were exposed to ultraviolet light up to 1 hr. Confirmation of suspected pesticidal residues was made by comparison with the standard. Also, R_{DDD} determinations were made.

RESULTS AND DISCUSSION

Findings in the study showed that three pesticidal residues were consistently present in the two potato types. These three pesticides were aldrin, heptachlor epoxide and endrin. Thin-layer chromatography was used for confirmation of the pesticidal residues. The pesticides extracted from the potatoes were compared to standards. The migration of the spots in question was the same as the standards. R_{DDD} values were determined and were found to be: aldrin 2.15, heptachlor epoxide 0.45, and endrin 0.26.

Averages of the actual quantities of these residues are presented in Tables A through G in the Appendix. Analyses of variance were calculated at the Louisiana State University Computer Science Center through the Department of Experimental Statistics. Six analyses were performed on the data. One analysis for each pesticide was done to determine if irradiation had a significant effect on the quantity of residues present in the control (Tables H, I, J of the Appendix). The remaining three analyses were used to determine the effects of storage, potato types, irradiation, and processing upon the quantities of pesticidal residues (Tables K, L, M of the Appendix).

Table 1 illustrates the average quantities and differences of the three pesticidal residues in unprocessed Irish and sweet potatoes. Irish potatoes contained an average of 1.10 ppm aldrin. The sweet potatoes contained significantly higher amounts (average of 1.31 ppm). Calculations showed this to be a 16.09% difference of aldrin in the two potato types. The statistical analysis (Table H) showed this to be a highly significant difference.

Table 1

Average Quantity[a] of Pesticidal Residues in Two Potato Types in Nonprocessed Potatoes

	Irish	Sweet	% Difference
Aldrin	1.10	1.31	16.09[b]
Heptachlor epoxide	1.26	1.16	8.03[b]
Endrin	97.68	96.69	1.02

[a]ppm

[b]highly significant difference ($P < 0.01$)

Heptachlor epoxide concentrations were also significantly different between the two potato types (Table I). As shown in Table 1, Irish potatoes contained an average of 1.26 ppm, whereas the sweet potatoes contained a lesser amount (1.16 ppm, average). There was an 8.03% difference between the two potato types. Although the percent difference of heptachlor epoxide in the potato types was only half that of aldrin, the difference was great enough to be a highly significant one.

Endrin in Irish and sweet potatoes differed an extremely small amount (1.02%). Since the potatoes were fortified with endrin, one would expect very little difference in the analysis of the nonprocessed potatoes. Irish potatoes contained an average of 97.68 ppm; sweet potatoes contained an average of 96.69 ppm.

The differences in pesticidal residue content of irradiated and nonirradiated, nonprocessed potatoes are shown in Table 2. Both aldrin and heptachlor epoxide showed a decreased residue content with irradiation. Irradiated potatoes had an average of 0.99 ppm and nonirradiated potatoes had a mean of 1.42 ppm, aldrin. This was a 30.1% difference in aldrin content. The analysis of variance (Table H) showed this difference to be highly significant. Irradiated potatoes had an average of 0.89 ppm, heptachlor epoxide and the nonirradiated samples contained 1.54 ppm, average. This was a 42.5% decrease of heptachlor epoxide. Table I shows this difference to be highly significant.

The amount of endrin in nonirradiated potatoes averaged 99.27 ppm. The irradiated samples contained 4.21% less endrin (95.10 ppm). Although Table J showed the difference to be nonsignificant, the difference approached significance ($P > 0.05$).

Table 2

Average Quantity[a] of Pesticidal Residues in Irradiated and Nonirradiated, Nonprocessed Potatoes

	Irradiated	Nonirradiated	% Difference
Aldrin	0.99	1.42	30.1[b]
Heptachlor epoxide	0.89	1.54	42.5[b]
Endrin	95.10	99.27	4.21

[a]ppm

[b]highly significant difference ($P < 0.01$)

Differences in processed potatoes are reported in Tables 3 through 9 with the effects of storage on the three pesticidal residues shown in Table 3.

There was a slight increase in aldrin from 0 to 6 weeks storage. The averages were 0.35 ppm and 0.40 ppm for 0 weeks and 6 weeks, respectively. This was an 11.82% increase. A considerable decrease in aldrin content was detected after 12 weeks storage (0.23 ppm). Compared to 0 weeks quantity of aldrin, there was a 34.5% decrease. Table K showing the analysis of variance of aldrin in processed potatoes, showed that a highly significant difference occurred during storage. Orthogonal comparisons (Table N) were performed to determine if one period of storage was superior to another. The first comparison of 0 versus 6 and 12 weeks storage indicated there was no difference in the residue content between nonstored and stored potatoes. However, when the 6 weeks storage was compared to the 12 weeks samples, the 34.5% decrease was highly significant. This suggested that potatoes containing aldrin must be stored more than six weeks before a significant quantity of the residue will be degraded.

Heptachlor epoxide had averages of 0.36 ppm, 0.42 ppm, and 0.46 ppm at 0, 6, and 12 weeks storage, respectively (Table 3). There was a 15.75% increase in the quantity of the residue between 0 and 6 weeks storage. Overall, between 0 and 12 weeks storage, there was a total increase of 22.5%. This increase was not a significant one (Table L). Orthogonal comparisons (Table O) detecting differences between 0 and 6 weeks storage showed that the increase was nonsignificant. Likewise, there was no significant change when the difference between 6 and 12

Table 3

Average Quantity[a] of Pesticidal Residues Throughout Three Storage Periods

	0 weeks	6 weeks	% Difference[b]	12 weeks	% Difference[b]
Aldrin	0.35	0.40	11.82	0.23	34.5[c]
Heptachlor epoxide	0.36	0.42	15.75	0.46	22.5
Endrin	42.40	47.95	11.58[c]	33.64	20.7[c]

[a]ppm

[b]compared to 0 weeks storage

[c]highly significant difference ($P < 0.01$)

week samples were compared. The consistent, nonsignificant increase in the heptachlor epoxide residue content can only be attributed to biological variation.

Endrin followed the trend of the other two pesticidal residues in that it showed an increase after 6 weeks storage. The 0 weeks samples had a mean of 42.40 ppm and increased 11.58% during storage for 6 weeks (47.95 ppm, average). After 12 weeks storage, the residue content of the potatoes was lowered to an average of 33.64 ppm. This was a 20.7% decrease over 12 weeks storage.

Table M showed that a highly significant change occurred in endrin residue quantities with storage. The orthogonal comparisons of Table P showed that the decrease in endrin residue content between 0 weeks compared to 6 and 12 weeks was significant. Also, there was a highly significant decrease in endrin residue content with 12 weeks storage, compared to the content at 6 weeks.

These results indicate that aldrin and endrin residues in potatoes can be significantly degraded if stored for an appropriate amount of time. Perhaps the heptachlor epoxide could also be significantly degraded if stored for longer periods. Lamb et al. (1968) used 5 month storage to initiate the degradation of DDT, parathion and carbaryl.

Table 4 compares the quantities of pesticidal residues in the two potato types after processing. Irish potatoes contained 0.40 ppm aldrin and sweet potatoes contained an average of 0.25 ppm of the residue. This was a difference of 37.6%. Table K showed this difference to be highly significant. In the control (Table 1) there was a 16.09% difference between the two potato types with sweet potatoes

Table 4

Average Quantity[a] of Pesticidal Residues in Processed Irish and Sweet Potatoes

	Irish	Sweet	% Difference
Aldrin	0.40	0.25	37.6[b]
Heptachlor epoxide	0.36	0.46	21.9[c]
Endrin	34.07	48.58	29.9[b]

[a]ppm

[b]highly significant difference ($P < 0.01$)

[c]significant difference ($P < 0.05$)

containing more aldrin than Irish potatoes. After processing, aldrin was found to a lesser degree in sweet potatoes. From the information it is believed that aldrin is more easily degraded in sweet potatoes than in Irish potatoes.

Heptachlor epoxide (Table 4) differed by 21.9% between the two potato types. Table L showed this difference to be a significant one. The Irish potatoes contained 0.36 ppm and the sweet potatoes contained an average of 0.46 ppm. In the control (Table 1) heptachlor epoxide residues were greater in Irish potatoes (1.26 ppm) than in the sweet potatoes (1.16 ppm), an 8.03% difference. Processing degreased the residue contents of both potato types. In the final results, however, there was a lesser amount of heptachlor epoxide residue in Irish than in sweet potatoes. This evidence indicates that processing is more effective in lowering the heptachlor epoxide residue level in Irish potatoes than in sweet potatoes.

After processing (Table 4) 34.07 ppm and 48.58 ppm, endrin were detected in Irish and sweet potatoes, respectively. This was a 29.9% difference between the two potato types. Table M showed the difference to be highly significant. In the control (Table 1) there was no statistical difference (1.02%) between the endrin residue levels in Irish and sweet potatoes. Processing not only lowered the pesticidal residue quantity, but it was also more effective with Irish potatoes than with sweet potatoes. This follows the pattern established by the other two pesticidal residues discussed previously. The food containing the residue played a significant role in the amount of pesticidal residue degradation. Endrin and heptachlor epoxide were

decreased to a greater extent in Irish potatoes; aldrin was decreased to a greater extent in sweet potatoes.

Table 5 shows the average quantity of pesticidal residues after irradiation of processed Irish and sweet potatoes. Irradiated potatoes contained 0.47 ppm aldrin; nonirradiated potatoes 0.18 ppm. This was a difference of 61.0%. Table K indicated this difference to be highly significant. This finding was contrary to what might be expected. The nonirradiated samples had a lower aldrin residue content than the irradiated samples. The control (Table 2) showed that irradiation without processing, significantly decreased the aldrin residue content in Irish and sweet potatoes. The only conclusion that could be drawn from the data was that irradiation in conjunction with processing offered a sparing effect on aldrin.

Heptachlor epoxide was detected as 0.46 ppm in irradiated potatoes and 0.36 ppm in nonirradiated potatoes. This was a difference of 22.6%. Table L showed the difference to be significant. As in the case of aldrin, heptachlor epoxide increased (22.6%) with irradiation. The control (Table 2) showed a 42.5% (highly significant) decrease with irradiation. The same conclusion as with aldrin was drawn for heptachlor epoxide. Apparently some other factor must influence the effect of irradiation on aldrin and heptachlor epoxide residues.

Irradiation (Table M) did not significantly affect endrin residues in the processed potatoes. There was a 3.5% decrease of the residue with irradiation. The mean of the irradiated group was 41.20 ppm whereas the nonirradiated group was 42.69 ppm. Irradiation did not significantly affect endrin in the control (Table 2) as it did for aldrin and heptachlor epoxide.

Table 5

Average Quantity[a] of Pesticidal Residues Resulting from Irradiation of Processed Irish and Sweet Potatoes

	Irradiated	Nonirradiated	% Difference
Aldrin	0.47	0.18	61.0[b]
Heptachlor epoxide	0.46	0.36	22.6[c]
Endrin	41.20	42.69	3.5

[a]ppm

[b]highly significant difference ($P < 0.01$)

[c]significant difference ($P < 0.05$)

Table 6 compared the effect of heat processing to freezing on pesticidal residue content of potatoes. Heat processing had a mean of 0.39 ppm aldrin and freezing had a mean of 0.26 ppm. This amounted to a 35.2% difference between the processing methods. Table K showed that there was a highly significant difference in pesticidal residue content with processing method. Orthogonal comparisons were performed to detect exactly where the differences occurred. The first comparison of Table Q compared the effects of heat processing to freezing on aldrin residue levels. Results showed that the 35.2% difference between the two processes was highly significant. Aldrin was significantly decreased with freezing.

Heat processed potatoes had a mean of 0.33 ppm heptachlor epoxide. An average of 0.50 ppm of the residue was detected in the frozen samples. There was a 34.4% difference between the two methods. Table L showed that there was not a significant difference on heptachlor epoxide content with processing. Table R illustrated the orthogonal comparison to detect differences between heat processing and freezing (first comparison). The difference was nonsignificant. Like aldrin, heptachlor epoxide was not significantly decreased by means of heat processing compared to freezing.

An average of endrin in the heat processed samples was 34.88 ppm; in the frozen samples it was 47.79 ppm. This was a difference of 27.0% in the residue contents. Table M showed that there existed a highly significant difference in endrin residues due to processing. Table S compared the effects of heat processing to the effects of freezing on endrin residue content. There was a highly significant

Table 6

Average Quantity[a] of Pesticidal Residues as a Result of Two Different Processing Applications

	Heat Processing	Freezing	% Difference
Aldrin	0.39	0.26	35.2[b]
Heptachlor epoxide	0.33	0.50	34.4[b]
Endrin	34.88	47.79	27.0[b]

[a]ppm

[b]highly significant difference ($P < 0.01$)

difference between the two basic processing methods. Heat processing was more effective for degradation of endrin.

Data indicated that one processing technique was not effective in degrading all pesticidal residues. Aldrin was more effectively degraded by freezing the samples. Endrin was degraded to a greater extent by heat processing. Heptachlor epoxide was equally affected by both processing methods.

Calculations were performed to determine if heat processing with water was more effective in pesticidal alterations than heat processing without water. The results are found in Table 7. Heat processing with water had a mean aldrin content of 0.47 ppm whereas the heat processed without water samples had a mean of 0.32 ppm. This was a 31.8% difference between the two processing methods. The second comparison of Table Q showed this difference to be highly significant. Freezing was the most effective method for lowering the aldrin residue content of potatoes (Table 6). A highly significant difference did exist, however, between heat processing with and without water (Table 7).

The second pesticidal residue, heptachlor epoxide, was present at a level of 0.35 ppm in the heat processes with water samples. An average of 0.31 ppm was detected in the heat processes without water group. A difference of 11.8% was calculated. The second orthogonal comparison of Table R showed this difference to be nonsignificant.

Potatoes heat processed with water had a mean endrin residue content of 32.41 ppm. The comparable group (heat processed without water) had a mean of 37.31 ppm. This amounted to a difference of 13.1%. The second comparison of Table S showed that the difference was

Table 7

Average Quantities[a] of Pesticidal Residues in Heat Processed Potatoes, with and without Water

	Heat Processed		
	Water	No Water	% Difference
Aldrin	0.47	0.32	31.8[b]
Heptachlor epoxide	0.35	0.31	11.8
Endrin	32.41	37.31	13.1[b]

[a]ppm

[b]highly significant difference ($P < 0.01$)

significant. Heat processing effected a significant decrease in the endrin residue content, compared to freezing (Table 6). Heat processing with and without water brought about significant alterations of the endrin residue levels; however heat processing with water was superior to heat processing without water.

Table 8 compared differences obtained by freezing blanched and unblanched potato samples. The frozen blanched group had an average of 0.22 ppm, aldrin and the frozen unblanched group had an average of 0.29 ppm. There was a 25.8% difference between the two groups. The third comparison of Table Q showed this difference to be nonsignificant.

Frozen blanched and frozen unblanched samples had an average of 0.47 and 0.53 ppm, heptachlor epoxide, respectively. A 12.1% difference existed between the two groups. Table Q illustrated that this difference was nonsignificant. Blanching prior to freezing did not effectively alter the heptachlor epoxide residue content.

Blanching before freezing reduced the amount of endrin in the samples more than did freezing alone. There was a mean of 44.70 ppm endrin in the blanched frozen group. The unblanched frozen group had a mean of 50.72 ppm, endrin. There was only an 11.9% difference between the two groups, but Table S (third comparison) showed that this difference was highly significant. Endrin was the only pesticidal residue of the three that had any significant changes due to blanching.

Summary of the Effects of Processing

Freezing was the most effective method of lowering the aldrin content in potatoes. Blanching was not necessary in this respect.

Table 8

Average Quantity[a] of Pesticidal Residues in Frozen, Blanched and Unblanched Potatoes

	Frozen		
	Blanched	Unblanched	% Difference
Aldrin	0.22	0.29	25.8
Heptachlor epoxide	0.47	0.53	12.1
Endrin	44.70	50.72	11.9[b]

[a]ppm

[b]highly significant difference ($P < 0.01$)

Heat processing without water was the next most effective method followed by heat processing with water.

Heptachlor epoxide was equally affected by all four of the processing methods. No one processing technique caused more degradation of the pesticidal residue than any other.

Endrin was most significantly altered by heat processing with water. Heat processing without water was the next most effective method. Blanching prior to freezing had a significant effect on the decrease of endrin levels.

SUMMARY

1. The purpose of this investigation was to determine if alterations of pesticidal residues could be produced in Irish and sweet potatoes with various processing methods.

2. Three residues were detected in the potatoes: aldrin, heptachlor epoxide and endrin.

3. Aldrin and endrin had to be stored 12 weeks before significant respective decreases of 34.5 and 20.7% occurred. Heptachlor epoxide was not affected by storage.

4. Irish and sweet potatoes had significant differences in pesticidal residue contents between the two potato types. There were differences of 37.6, 21.9 and 29.9% of aldrin, heptachlor epoxide and endrin, respectively.

5. Irradiation did not decrease the residue contents of processed potatoes. However, irradiation of the nonprocessed potatoes resulted in a 30.1, 42.5 and 4.21% decrease of aldrin, heptachlor epoxide and endrin, respectively. Aldrin and heptachlor epoxide decreases were highly significant.

6. Heat processing compared to freezing methods showed that aldrin was significantly decreased (35.2%) by freezing. Endrin was significantly decreased (27.0%) by heat processing. There was no significant difference in the heptachlor epoxide residue content between the two processing techniques.

7. Aldrin was significantly decreased (31.8%) by heat processing without water, when comparing heat processing, with and without water. Heptachlor epoxide was not affected. Endrin was significantly decreased (13.1%) by heat processing with water.

8. When comparing freezing, with and without blanching, it was found that aldrin and heptachlor epoxide were not significantly altered. Endrin was significantly altered (11.9%) by blanching before freezing.

9. Thin-layer chromatography of the extracted residues compared favorably in R_{DDD} values to the standards.

BIBLIOGRAPHY

Beasley, T. H., Sr. and H. W. Ziegler. 1970. Chlorinated pesticide residue analysis of spinach extracts using silicic acid-glass fiber sheet instead of the usual Florisil column for the cleanup operation. A Seminar. Pittsburgh Conference in Analytical Chemistry. Cleveland, Ohio.

Blinn, R. C. and F. A. Gunther. 1962. Pesticides Research Bulletin, Stanford Research Institute. Vol. 2, No. 3.

Blinn, R. C. and F. A. Gunther. 1962a. Pesticides Research Bulletin, Stanford Research Institute. Vol. 2, No. 4.

Blinn, R. C. and F. A. Gunther. 1963. Pesticides Research Bulletin, Stanford Research Institute. Vol. 3, No. 1.

Blinn, R. C. 1963. Thin-layer chromatographic isolation and infrared or colorimetric identification of thimet residues. J.A.O.A.C. 46, 952.

Bonner, F. 1968. Summary of pesticide residue analysis methods. Harry D. Wilson Laboratories, Louisiana State University, Baton Rouge.

Burke, J. and W. Holswade. 1964. Gas chromatography with micro-coulometric detection for pesticide residue analysis. J.A.O.A.C. 47, 845.

Carlin, A. F., E. T. Hibbs and P. A. Dahm. 1966. Insecticide residues and sensory evaluation of canned and frozen snap beans field-sprayed with guthion and DDT. J. Food Tech. 20, 80.

Claborn, H. V. and R. W. Wells. 1952. Methoxychlor, DDT, CS-708 and dieldrin — their rates of excretion in milk. Agr. Chem. 7, (10), 28.

Coffin, E. E. and W. P. McKinley. 1963. Determination of parathion, methyl parathion, epm, and their oxons in some fruit and vegetable crops. J.A.O.A.C. 46, 223.

Elkins, E. R., F. C. Lamb, R. P. Farrow, R. W. Cook, M. Kawai and J. R. Kimball. 1968. Removal of DDT, malathion, and carbaryl from green beans by commercial and home preparative procedures. Agri. and Food Chem. 16, 962.

Ely, R. E., L. A. Moore, R. H. Carter, P. E. Hubanks and F. W. Poos. 1954. Excretion of dieldrin in the milk of cows fed dieldrin-sprayed forage and technical dieldrin. J. Dairy Sci. 37, 1461.

Farrow, R. P., E. R. Elkins, Jr. and R. W. Cook. 1966. Conversion of DDT to TDE in canned spinach. Agri. and Food Chem. 14, 430.

Farrow, R. P., F. C. Lamb, R. W. Cook, J. R. Kimball and E. R. Elkins. 1968. Removal of DDT, malathion, and carbaryl from tomatoes by commercial and home preparative methods. Agri. and Food Chem. 16, 65.

Fleck, E. E. and H. L. Haller. 1946. Stability of DDT and related compounds. J. Am. Chem. Soc. 68, 142.

Gannon, N., R. P. Link and G. C. Decker. 1959. Storage of dieldrin in tissues and its excretion in milk of dairy cows fed dieldrin in their diets. Agri. and Food Chem. 7, 824.

Giuffrida, L. and F. Ives. 1964. Investigation of two gas chromatographic techniques for the determination of organophosphate pesticide residues. J.A.O.A.C. 47, 1112.

Glotfelty, D. E. and J. H. Caro. 1970. Artifacts of dieldrin in gas chromatographic analysis of green plant material. Anal. Chem. 42, 282.

Gorbach, S. and U. Wagner. 1967. Pentachloronitrobenzene residues in potatoes. Agri. and Food Chem. 15, 654.

Hallab, A. H. 1968. Detoxification of pesticidal residues in fish and shellfish. A Ph.D. dissertation. Louisiana State University, Baton Rouge.

Harris, J. R., G. E. Stoddard, G. Q. Bateman, J. L. Shupe, D. A. Greenwood, L. E. Harris, T. L. Bahler and F. V. Liebermann. 1956. Effect of feeding dieldrin- and heptachlor-treated alfalfa hay to dairy cows. Agri. and Food Chem. 4, 694.

Hemphill, D. D., R. E. Baldwin, A. Deguzman and H. K. Deloach. 1967. Effects of washing, trimming, and cooking on levels of DDT and derivatives in green beans. Agri. and Food Chem. 15, 290.

Henderson, G. L. and D. G. Crosby. 1968. The photodecomposition of dieldrin residues in water. Bull. of Environ. Contam. and Toxicology. 3, 131.

Ives, N. F. and L. Giuffrida. 1967. Investigation of thermionic detector response for the gas chromatography of P, N, As, and Cl organic compounds. J.A.O.A.C. 50, 1.

Kilgore, L. and F. Windham. 1970. Disappearance of malathion residue in broccoli during cooking and freezing. Agri. and Food Chem. 18, 162.

Lamb, F. C., R. P. Farrow, E. R. Elkins, R. W. Cook and J. R. Kimball. 1968. Behavior of DDT in potatoes during commercial and home preparation. Agri. and Food Chem. 16, 272.

Lamb, F. C., R. P. Farrow, E. R. Elkins, J. R. Kimball and R. W. Cook. 1968. Removal of DDT, parathion, and carbaryl from spinach by commercial and home preparative methods. Agri. and Food Chem. 16, 967.

Langois, B. E., A. R. Stemp and B. J. Liska. 1964. Rapid cleanup of dairy products for analysis of chlorinated insecticide residue by electron capture gas chromatography. Agri. and Food Chem. 12, 243.

Lovelock, J. E. and S. R. Lipsky. 1960. Electron affinity spectroscopy- a new method for the identification of functional groups in chemical compounds separated by gas chromatography. J. Am. Chem. Soc. 82, 431.

Mattick, L. R., D. L. Barry, F. M. Antenucci and A. W. Avens. 1963. The disappearance of endrin residues on cabbage. Agri. and Food Chem. 11, 54.

Morley, H. V. and M. Chiba. 1964. Thin-layer chromatography for chlorinated pesticide residue analysis without cleanup. J.A.O.A.C. 47, 306.

Morris, W. W., Jr. and E. O. Haenni. 1963. Infrared spectra of pesticides. J.A.O.A.C. 46, 964.

Payne, W. R., Jr. and W. S. Cox. 1966. Micro-infrared analysis of dieldrin, endrin, and other chlorinated pesticide residues in complex substrates. J.A.O.A.C. 49, 989.

Saha, J. G., M. A. Nielsen and A. K. Sumner. 1970. Effect of commercial processing techniques on lindane- and DDT- ^{14}C residues in rapeseed oil. Agri. and Food Chem. 18, 43.

Schmit, J. A., U. J. Peters and M. A. Loskaris. 1963. A rapid method for the determination of pesticide residues in tomatoes and tomato products. Presented at Annual Meeting of the AOAC. Washington, D. C.

Snedecor, G. W. 1967. Statistical methods. 5th Edition. Iowa State University Press.

Susi, H. and H. E. Rector. 1958. Quantitative infrared analysis of pesticides in the solid state. Anal. Chem. 30, 1933.

Watts, J. O. and A. K. Klein. 1962. Determination of chlorinated pesticide residues by electron-capture gas chromatography. J.A.O.A.C. 45, 102.

Weiss, J. 1952. Chemical dosimetry using ferrous and ceric sulfates. Nucleonics. 10, 28.

Westlake, A., W. E. Westlake and F. A. Gunther. 1970. Determination of Residues of GC-9160 in Cabbage, Lettuce, and Citrus Fruit. Agri. and Food Chem. 18, 159.

APPENDIX

Table A

Average Quantity[a] of Pesticidal Residues in Nonprocessed Potatoes[b]

	Irish		Sweet	
	Irradiated	Nonirradiated	Irradiated	Nonirradiated
Aldrin	0.99	1.20	0.99	1.63
Heptachlor epoxide	0.91	1.62	0.86	1.46
Endrin	95.78	99.57	94.41	98.97

[a]ppm

[b]mean of four replications

Table B

Quantities[a] of Pesticidal Residues in Irish Potatoes, 0 weeks Storage[b]

	Irradiated				Nonirradiated			
	Heat Processed		Frozen		Heat Processed		Frozen	
	Water	No water	Blanched	Unblanched	Water	No water	Blanched	Unblanched
Aldrin	0.95	0.40	0.56	0.31	0.36	0.15	0.27	0.28
Heptachlor epoxide	0.34	0.28	0.19	0.15	0.21	0.06	0.44	0.50
Endrin	24.12	3.05	41.10	31.35	26.95	26.68	49.48	79.83

[a]ppm

[b]mean of four replications

Table C

Quantities[a] of Pesticidal Residues in Irish Potatoes, 6 Weeks Storage[b]

	Irradiated				Nonirradiated			
	Heat Processed		Frozen		Heat Processed		Frozen	
	Water	No water	Blanched	Unblanched	Water	No water	Blanched	Unblanched
Aldrin	0.42	0.51	0.67	0.72	0.32	0.55	0.38	0.26
Heptachlor epoxide	0.00	0.17	0.33	0.48	0.19	0.42	0.31	0.51
Endrin	25.46	23.37	43.02	61.48	41.89	35.74	64.01	66.72

[a]ppm

[b]mean of four replications

Table D

Quantities[a] of Pesticidal Residues in Irish Potatoes, 12 Weeks Storage[b]

	Irradiated				Nonirradiated			
	Heat Processed		Frozen		Heat Processed		Frozen	
	Water	No water	Blanched	Unblanched	Water	No water	Blanched	Unblanched
Aldrin	0.78	0.66	0.00	1.07	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.54	0.66	0.27	1.49	0.37	0.18	0.23	0.50
Endrin	46.91	44.39	7.50	57.15	7.04	1.24	1.63	7.61

[a] ppm

[b] mean of four replications

Table E

Quantities[a] of Pesticidal Residues in Sweet Potatoes, 0 Weeks Storage[b]

	Irradiated				Nonirradiated			
	Heat Processed		Frozen		Heat Processed		Frozen	
	Water	No water	Blanched	Unblanched	Water	No water	Blanched	Unblanched
Aldrin	0.71	0.31	0.03	0.70	0.46	0.00	0.00	0.13
Heptachlor epoxide	0.37	0.29	1.13	0.58	0.26	0.00	0.33	0.55
Endrin	50.80	30.57	74.96	69.00	42.51	31.26	36.16	60.53

[a]ppm

[b]mean of four replications

Table F

Quantities[a] of Pesticidal Residues in Sweet Potatoes, 6 Weeks Storage[b]

	Irradiated				Nonirradiated			
	Heat Processed		Frozen		Heat Processed		Frozen	
	Water	No water	Blanched	Unblanched	Water	No water	Blanched	Unblanched
Aldrin	0.40	0.33	0.55	0.00	1.24	0.00	0.00	0.00
Heptachlor epoxide	0.50	0.39	0.69	0.43	0.61	0.61	0.58	0.53
Endrin	36.14	34.84	52.02	41.32	63.97	58.01	54.96	64.16

[a]ppm

[b]mean of four replications

Table G

Quantities[a] of Pesticidal Residues in Sweet Potatoes, 12 Weeks Storage[b]

	Irradiated				Nonirradiated			
	Heat Processed		Frozen		Heat Processed		Frozen	
	Water	No water	Blanched	Unblanched	Water	No water	Blanched	Unblanched
Aldrin	0.00	0.93	0.15	0.08	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.43	0.60	0.57	0.27	0.35	0.00	0.51	0.37
Endrin	2.00	89.33	57.66	41.39	21.17	69.24	53.89	30.14

[a]ppm

[b]mean of four replications

Table H

Analysis of Variance of Aldrin in Nonprocessed and Irradiated Potatoes

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
Total	15	1.1671		
Potatoes	1	0.1771	0.1771	27.2307**
Irradiation	1	0.7260	0.7260	111.6923**
Potatoes x Irradiation	1	0.1854	0.1854	28.5230**
Error	12	0.0786	0.0065	

**$P < 0.01$

Table I

Analysis of Variance of Heptachlor Epoxide in Nonprocessed and Irradiated Potatoes

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
Total	15	1.8539		
Potatoes	1	0.0411	0.0411	5.9600**
Irradiation	1	1.7170	1.7170	247.8000**
Potatoes x Irradiation	1	0.0124	0.0124	1.75
Error	12	0.0833	0.0069	

**P < 0.01

Table J

Analysis of Variance of Endrin in Nonprocessed and Irradiated Potatoes

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
Total	15	0.0148	0.0012	
Potatoes	1	0.0004	0.0004	0.2352
Irradiation	1	0.0070	0.0070	4.1176
Potatoes x Irradiation	1	0.0001	0.0001	0.0588
Error	12	0.0209	0.0017	

Table K

Analysis of Variance of Aldrin in Processed Potatoes

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
Total	191	28.5421		
Weeks	2	0.9213	0.4607	9.1590**
Potatoes	1	1.0049	1.0049	19.9781**
Weeks x Potatoes	2	0.0927	0.0471	0.9363
Irradiation	1	4.3724	4.3724	86.9624**
Potatoes x Irradiation	1	0.3314	0.3314	6.5884**
Weeks x Irradiation	2	1.0911	0.5456	10.8469**
Weeks x Potatoes x Irradiation	2	0.3878	0.1939	3.5848*
Process	3	1.3534	0.4511	8.9681**
Irradiation x Process	3	0.5235	0.1745	3.4691*
Potato x Process	3	0.5614	0.1871	3.7196*
Potato x Process x Irradiation	3	1.6610	0.5537	11.0079**
Weeks x Process	6	2.3798	0.3966	7.8846**
Weeks x Irradiation x Process	6	2.0654	0.3442	6.8429**
Weeks x Potatoes x Process	6	3.2568	0.5428	10.7912**
Weeks x Potatoes x Irradiation x Process	6	1.2815	0.2136	4.2465**
Error	144	7.2558	0.0503	

*P < 0.05
**P < 0.01

Table L

Analysis of Variance of Heptachlor Epoxide in Processed Potatoes

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
Total	191	28.0117		
Weeks	2	0.3526	0.1763	1.6790
Potatoes	1	0.3732	0.3732	3.5542
Weeks x Potatoes	2	1.3354	0.6677	6.3590**
Irradiation	1	0.5273	0.5273	5.0228*
Potatoes x Irradiation	1	0.0250	0.0250	0.0238
Weeks x Irradiation	2	1.1995	0.5998	5.7123**
Weeks x Potatoes x Irradiation	2	0.7954	0.3977	3.7876*
Process	3	0.1544	0.0515	0.4904
Irradiation x Process	3	0.1679	0.0560	0.5333
Potato x Process	3	0.1536	0.5119	4.8752**
Potato x Process x Irradiation	3	0.6304	0.2101	2.0009
Weeks x Process	6	0.8546	0.1424	1.3561
Weeks x Irradiation x Process	6	1.1889	0.1981	1.8876
Weeks x Potatoes x Process	6	1.3058	0.2176	2.0723
Weeks x Potatoes x Irradiation x Process	6	1.0398	0.1733	1.6504
Error	144	15.1360	0.1050	

*P < 0.05
**P < 0.01

Table M

Analysis of Variance of Endrin in Processed Potatoes

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
Total	191	1090.1030		
Weeks	2	66.4575	33.2287	26.9123**
Potatoes	1	101.1044	101.1044	81.8858**
Weeks x Potatoes	2	27.3490	13.6745	11.0751**
Irradiation	1	0.0309	0.0309	0.0250
Potatoes x Irradiation	1	0.0317	0.0317	0.0256
Weeks x Irradiation	2	104.9619	52.4810	42.5050**
Weeks x Potatoes x Irradiation	2	86.5080	43.2540	35.0319**
Process	3	95.1759	31.7253	25.6946**
Irradiation x Process	3	2.1507	0.7169	0.5806
Potato x Process	3	62.4314	20.8105	16.8547**
Potato x Process x Irradiation	3	25.3339	8.4447	6.8394**
Weeks x Process	6	160.8501	26.8083	21.7123**
Weeks x Irradiation x Process	6	52.1868	8.6978	7.0444**
Weeks x Potatoes x Process	6	114.6609	19.1101	15.4775**
Weeks x Potatoes x Irradiation x Process	6	13.0580	2.1763	1.7026
Error	144	177.8093	1.2347	

**P <0.01

Table N

Orthogonal Comparisons of Effects of Storage on Aldrin

Source	Degrees of Freedom	Mean Squares	F
1 vs. 2, 3	1	0.0286	0.5685
2 vs. 3	1	0.8944	12.0258**
Error	144	0.0503	

**P <0.01

1 = 0 weeks storage
2 = 6 weeks storage
3 = 12 weeks storage

Table 0

Orthogonal Comparisons of Effects of Storage on Heptachlor Epoxide

Source	Degrees of Freedom	Mean Squares	F
1 vs. 2, 3	1	0.3088	2.9409
2 vs. 3	1	0.0438	0.4171
Error	144	0.1050	

1 = 0 weeks storage
2 = 6 weeks storage
3 = 12 weeks storage

Table P

Orthogonal Comparisons of Effects of Storage on Endrin

Source	Degrees of Freedom	Mean Squares	F
1 vs. 2, 3	1	6.3693	5.1585*
2 vs. 3	1	60.0882	48.6662**
Error	144	1.2347	

*P < 0.05
**P < 0.01

1 = 0 weeks storage
2 = 6 weeks storage
3 = 12 weeks storage

Table Q

Orthogonal Comparisons of Effects of Processes on Aldrin

Source	Degrees of Freedom	Mean Squares	F
1, 2 vs. 3, 4	1	0.7807	15.5208**
1 vs. 2	1	0.5353	10.6421**
3 vs. 4	1	0.0680	1.3518
Error	144	0.0503	

**P < 0.01

1 = Heat processed with water
2 = Heat processed without water
3 = Blanched and frozen
4 = Unblanched and frozen

Table R

Orthogonal Comparisons of Effects of Processes on Heptachlor Epoxide

Source	Degrees of Freedom	Mean Squares	F
1, 2 vs. 3, 4	1	0.1403	1.3361
1 vs. 2	1	0.0045	0.0428
3 vs. 4	1	0.0098	0.0933
Error	144	0.1050	

1 = Heat processed with water
2 = Heat processed without water
3 = Blanched and frozen
4 = Unblanched and frozen

Table S

Orthogonal Comparisons of Effects of Processes on Endrin

Source	Degrees of Freedom	Mean Squares	F
1, 2 vs. 3, 4	1	80.2992	65.0353**
1 vs. 2	1	5.7652	4.6693*
3 vs. 4	1	9.1905	7.4435*
Error	144	1.2347	

*P <0.05
**P <0.01

1 = Heat processed with water
2 = Heat processed without water
3 = Blanched and frozen
4 = Unblanched and frozen

VITA

James M. Solar, son of Mr. and Mrs. Henry J. Solar, Sr., was born in Baton Rouge, Louisiana, on January 3, 1943. He was educated in the parochial and public schools of Baton Rouge, Louisiana, and was graduated from Istrouma Senior High School in 1960. In June of the same year he entered Louisiana State University. After two years of study he transferred to Southeastern Louisiana College and was graduated in January, 1965 with a Bachelor of Science Degree in Biology. He remained at Southeastern Louisiana College as a special student and a laboratory instructor for one semester. In June, 1965, he entered the Department of Food Science and Technology at Louisiana State University and was granted a graduate assistantship. He received his Master of Science degree in January, 1968. He is presently a candidate for the degree of Doctor of Philosophy in Food Science with a minor in Foods and Nutrition.

EXAMINATION AND THESIS REPORT

Candidate: JAMES MICHAEL SOLAR

Major Field: Food Science

Title of Thesis: Pesticidal Residue Alterations in Potatoes During Processing.

Approved:

Joseph A. Lingo
Major Professor and Chairman

Max Deadrick
Dean of the Graduate School

EXAMINING COMMITTEE:

A. F. Novak

Robert M. Grodner

William J. McKnight

M. R. Ramachandra Rao

Fred H. Hoskins

Date of Examination:

May 8, 1970